



Docket No.: 211827US0CONT

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

RE: Application Serial No.: 09/923,353
Applicants: Philippe BOIRE, et al.
Filing Date: August 8, 2001
For: SUBSTRATE WITH A PHOTOCATALYTIC
COATING
Group Art Unit: 1771
Examiner: A.T. PIZIALI

SIR:

Attached hereto for filing are the following papers:

APPEAL BRIEF

Our credit card payment form in the amount of **\$500.00** is attached covering any required fees. In the event any variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 15-0030. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

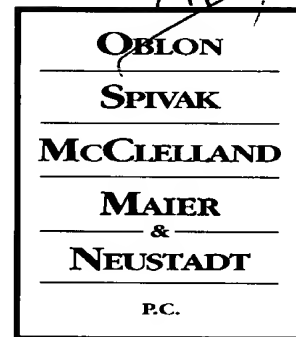
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III. STATUS OF THE CLAIMS

The appealed claims are Claims 25-30, 34-39, 44 and 45, the only claims in the case.

Claims 1-24, 31-33, 40-43 and 46 are canceled.

IV. STATUS OF AMENDMENTS

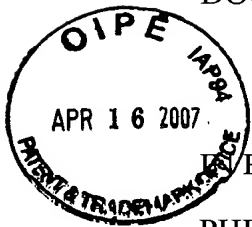
No amendments have been submitted subsequent to the mailing of the Office Action on November 14, 2006.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

Claim 25 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having photocatalytic properties {page 2, lines 13-14}, and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, and obtained by thermal decomposition of titanium precursors selected from the group consisting of organo-metallic precursors and metallic halide precursors {page 13, lines 9-34}, wherein said coating has a thickness between 5 and 50 nm {page 18, line 14}, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm {page 3, lines 18-24 and page 26, lines 19-23}.

Claim 26 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having a photocatalytic properties {page 2, lines 13-14}, and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, and a thin layer forming a barrier to alkali metals originating from the substrate, and located between said substrate and said coating {page 14, line 34 to page 15, line 5}, wherein the

DOCKET NO: 211827US0CONT



IN THE UNITED STATES PATENT & TRADEMARK OFFICE

RE APPLICATION OF :

PHILIPPE BOIRE, ET AL. :

EXAMINER: A.T. PIZIALI

SERIAL NO: 09/923,353 :

FILED: AUGUST 8, 2001 :

GROUP ART UNIT: 1771

FOR: SUBSTRATE WITH A PHOTOCATALYTIC COATING

APPEAL BRIEF

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

This is an appeal from the Final Rejection of the claims dated November 14, 2006.

I. REAL PARTY IN INTEREST

The real party in interest is Saint-Gobain Glass France.

II. RELATED APPEALS AND INTERFERENCES

Appeals have been filed in U.S. application serial Nos. 10/079,483 and 10/419,872.

Appellants, Appellants' legal representative and their assignee are not aware of any other appeals or interferences which will directly affect or be directly affected by or having a bearing on the Board's decision in this appeal.

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crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm {page 3, lines 18-24 and page 26, lines 19-23}.

Claim 27 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having photocatalytic properties {page 2, lines 13-14}, and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, and wherein said coating is hydrophilic {page 6, lines 11-26}, and has a contact angle with water below 5 after exposure to luminous rays {page 6, lines 23-26}, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 1000 nm {page 3, lines 18-24 and page 26, lines 19-23}.

Claim 28 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having photocatalytic properties {page 2, lines 13-14}, and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, and wherein said coating has a root mean square (RMS) rugosity between 2 and 20 nm {page 8, lines 3-6}, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm {page 3, lines 18-24 and page 26, lines 19-23}.

Claim 29 is directed to a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least one of its faces with a coating having photocatalytic properties {page 2, lines 13-14} and containing at least partially crystalline titanium oxide {page 2, lines 14-15 and page 3, lines 2-3} and having a thickness between 10 and 80 nm {page 8, lines 29-33}.

Claim 34 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having photocatalytic properties {page 2, lines 13-14} and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, wherein

said coating contains also at least one oxide with a lower refractive index than titanium oxide {page 4, lines 11-16}, the titanium content of the coating being at least 40%, by weight with respect to the total weight of oxides in the coating {page 4, lines 25-29}.

Claim 36 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least a portion of one of its faces with a coating having photocatalytic properties {page 2, lines 13-14} and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}, wherein there is at least a layer arranged between the substrate and said coating, said layer being electrically conductive {page 9, lines 21-25}.

Claim 38 is directed to an electrically controlled variable absorption glazing {page 12, lines 23-34} wherein at least one of the external faces of said glazing is provided with a coating having photocatalytic properties {page 2, lines 13-14} and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}.

Claim 39 is directed to a windshield {page 11, line 36} wherein at least the face of said windshield turned toward the inside of the passenger compartment is provided with a coating having photocatalytic properties {page 2, lines 13-14} and comprising titanium oxide at least partly crystallized in the anatase form {page 2, lines 14-15 and page 3, lines 2-3}.

Claim 44 is directed to a coated substrate which is a glass, ceramic or vitroc ceramic substrate {page 2, lines 10-11} provided on at least one of its faces with a coating with photocatalytic properties {page 2, lines 13-14}, containing titanium oxide {page 2, line 14-15} and doped by at least one metal selected from the group consisting of Nb, Ta, Fe, Bi, Co, Ni, Cu, Rh, Ce, and Mo {page 5, lines 11-16}.

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

1. Whether claims 25-27, 29-30, and 34-36 are unpatentable under 35 U.S.C. §102(e) or §103(a) over Vandiest (U.S. patent No. 5,721,054).
2. Whether claims 26-28 and 44-45 are unpatentable under 35 U.S.C. §102(e) or §103(a) over Kato (U.S. patent No. 6,284,314).
3. Whether claim 38 is unpatentable under 35 U.S.C. §103(a) over Vandiest in view of any one of Ito et al. (U.S. patent No. 4,664,934), Lynam et al. (U.S. patent No. 5,076,673) or Weppner et al. (U.S. Patent No. 5,202,788).
4. Whether claim 39 is unpatentable under 35 U.S.C. §103(a) over Vandiest.
5. Whether claims 25-30, 34-37, 39 and 44-45 are unpatentable under 35 U.S.C. §103(a) over Plumet et al. (U.S. patent No. 3,984,591) in view of any one of Vandiest or Kato.
6. Whether claim 38 is unpatentable Under 35 U.S.C. §103(a) over Plumet in view of any one of Vandiest or Kato and in view of any one of Ito, Lynam or Weppner.

VII. ARGUMENT

1. Claims 25-27, 29-30, and 34-36 Are Not Unpatentable Under 35 U.S.C. §102(e) or §103(a) Over Vandiest (U.S. patent No. 5,721,054).

Appellants submitted a second executed Rule 132 Declaration from Dr. Bernard Nghiem on May 22, 2006. Dr. Nghiem has read and is familiar with the specification and the subject matter of claims 25-30, 34-39 and 44-45 of the present application (see paragraphs 4-6 of the second Declaration).

Dr. Nghiem has carefully reviewed the description of the coating in the specification (see paragraph 7 of the second Declaration). Based on that review, Dr. Nghiem concludes that:

In view of the description provided by the specification of the above-identified application, one skilled in the art would have concluded that the coating of the invention described therein and specified in the claims identified above was mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing. [See paragraph 8 of the second Declaration; emphasis added]

Dr. Nghiêm acknowledges that the specification does not contain explicitly state that the coating is mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing. However, he states:

...for the reasons discussed above, one skilled in the art reading that specification would appreciate that the coating of the substrates specified in claims 25-30, 34-39 and 44-45 of the above-identified application necessarily had those properties in order to be used as a glazing in the specification. [See paragraph 9 of the second Declaration.]

Appellants submitted the first executed Rule 132 Declaration from Dr. Nghiêm on November 23, 2005. In that Declaration, Dr. Nghiêm discusses that procedure for depositing titanium oxide coatings. See the top of page 2 of the first Declaration. Dr. Nghiêm states:

After closely examining the deposition procedure described by Vandiest, I believe that, while the conditions given by Vandiest can work well with a mixture of tin tetrachloride and water, this is not the case for titanium tetrachloride and water. On the basis of experiments I performed, I can confirm that for the deposition of titania, the use of the $TiCl_4$ and water ends up creating a nanoparticle powder and does not form a homogeneous coating on the substrate surface. [See page 2 of the first Declaration.]

Dr. Nghiêm points out attempting to deposit titanium dioxide under the conditions described by Vandiest produces the well-known result of creating powder as had been used in fluid flows to study the hydrodynamics of the flow (see the bottom of page 2 and the top of page 3 of the first Declaration).

Beginning at the bottom of page 3 of the first Declaration, Dr. Nghiêm describes the deposition procedures as described in patents referred to by Vandiest in the specification of the patent. Dr. Nghiêm states

If such a configuration (in figure 3) is used with water and titanium tetrachloride, at the intersection region between the 2 flows from the 2 nozzles, nano powder is formed instead of a coating. [Declaration page 3, last sentence.]

So if this kind of tool is used with TiCl_4 and water instead of SiH_4 and O_2 , nano power is formed before arriving on the substrate surface. [Declaration page 4, last sentence.]

Beginning at page 6 of the first Declaration, Dr. Nghiêm describes experiments that were conducted in order to reproduce the conditions of the deposition and the tool for the gas injection mentioned by Vandiest and FR2648453. Dr. Nghiêm summarizes the results of the experiments at the top of page 9, stating:

With the preceding deposition parameters, we could not deposit any real coating. Instead, we have produced powder, part of which weakly adheres to the surface of the substrate when the experiment was over. This powder can be easily wiped out by a tissue cloth.

Dr. Nghiêm concludes as follows:

The process parameters described by Vandiest for the deposition of large gap semi conductor like SnO_2 or TiO_2 , starting from Ti or Sn tetrachloride with water as oxidant are only valid for the deposition of SnO_2 . In the case of TiO_2 , our own experiments and several scientific sources have proven clearly that even at low temperature TiO_2 powder is formed when TiCl_4 and water is brought into contact, instead of an homogeneous coating on the surface. [Declaration at the middle of page 9.]

Thus, the Declaration of Dr. Nghiêm demonstrates that the method described in Example 1 of Vandiest does not produce a photocatalytic coating of titanium dioxide on a substrate.

In fact, in Dr. Nghiêm's second Declaration he states:

For those reasons, the process parameters described by Vandiest do not provide a coating of photocatalytic titanium oxide that is mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing as specified in claims 25-30, 34-39 and 44-45 of the above-identified application. [See paragraph 11 of the second declaration.]

Appellants submitted an executed Rule 132 Declaration from Dr. Léthicia Guéneau on December 8, 2003. Dr. Guéneau has eight years of experience in the field of physico chemistry/self-cleaning glass (see paragraphs (1) and (2) of the Declaration).

Dr. Guéneau points out that in Example 2, Vandiest describes a glass substrate coated with a 41 nm TiO₂ layer, which, in turn, is coated with a layer of Fe, Co, and Cr oxides having a thickness of 45 nm (see paragraph (6) of the Declaration). In Example 3, Vandiest describes a glass substrate coated with a 85 nm TiO₂ layer, which, in turn, is coated with a layer of Fe, Co, and Cr oxides having a thickness of 46.5 nm (see paragraph (7) of the Declaration). According to Dr. Guéneau, Fe, Co, and Cr oxides are well-known to be poisons for photocatalysts. Therefore, one of ordinary skill in the art would limit the contents of those metal oxides because of their known properties as photocatalyst poisons (see paragraph (8) of the Declaration).

The Examiner asserts that the analysis provided by Dr. Guéneau is contradicted by the specification of the present application and Kato (see the Examiner's Answer dated April 27, 2004 at page 10, first full paragraph). This is not the case. That this is so is demonstrated by Carneiro et al., Study of the Deposition Parameters and Fe-Dopant Effect in the Photocatalytic Activity of TiO₂ Films Prepared by dc Reactive Magnetron Sputtering, *Vacuum*, 78, 2005, pp. 37-46, a copy of which was cited on May 22, 2006. Carneiro et al. describe the effect of doping a photocatalytic coating of TiO₂ on a substrate with iron. At a low concentration of iron, the layer has higher photocatalytic activity as compared to the undoped layer. In contrast, a highly-doped layer has strongly decreased photocatalytic activity. In view of the foregoing, Dr. Guéneau's comments are not inconsistent with the specification of the present application and Kato.

In addition, in Examples 2 and 3, the TiO₂ layer is buried under the Fe-Co-Cr layer. For that reason, one would expect that accumulated organic matter could not be decomposed by the TiO₂ layer because it would never get to that layer. Therefore, such a layer is not photocatalytic as recited in the claims of the present application.

Referring to the Examiner's comments at the first full paragraph at page 13 of the Office Action dated November 14, 2006, the Declarations discussed above address both embodiments described in Vandiest. The two Declarations submitted by Dr. Nghiêm address the embodiment where the TiO₂ layer is on the surface, i.e., the non-absorbent layer is on the absorbent layer. The Declaration from Dr. Guéneau addresses the embodiment in which the TiO₂ layer is on the bottom, i.e., the absorbent layer is on the non-absorbent layer.

In view of the foregoing, Vandiest fails to describe or suggest the claimed coated substrate. Accordingly, withdrawal of these grounds of rejection is respectfully requested.

2. Claims 26-28 and 44-45 Are Not Unpatentable Under 35 U.S.C. §102(e) or §103(a) Over Kato (U.S. patent No. 6,284,314).

Dr. Guéneau notes that Kato is completely silent regarding the size of titanium oxide crystallites (see paragraph (15) of the Declaration). According to Dr. Guéneau, Kato also fails to suggest that the titanium crystallites have an average size of between 60 and 100 nm, since the reference fails to even mention titanium crystallites at all. See paragraph (18) of the Declaration.

According to Dr. Guéneau, the reference also fails to describe the contact angle or the root mean square (RMS) rugosity of the coating (see paragraph (16) of the Declaration). In Dr. Guéneau's opinion, Kato is completely silent with respect to the RMS rugosity of the coating and, therefore, fails to suggest a coating having a value between 2 and 20 nm. See paragraph (21) of the Declaration.

Dr. Guéneau also points out that Kato fails to explicitly disclose a layer which functions as a barrier to alkali metals originating from the substrate, and that the reference does not suggest that such a component would be desirable. See paragraph (19) of the Declaration. In addition, Dr. Guéneau points out that Kato describes the optional heating of solutions coated on substrates in the absence of a barrier layer to alkalis, such as sodium from the substrate. Quartz glass substrates are described, which consist of SiO_2 , and do not contain alkalis. See paragraph (22) of the Declaration.

Claim 26 recites, *inter alia*, (1) a thin layer a thin layer forming a barrier to alkali metals originating from the substrate, which is located between the substrate and the coating, and (2) that the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm. Kato does not identify a layer which functions as a barrier to alkali metals originating from the substrate, nor does the reference suggest that such a component would be desirable. Kato fails to suggest that the titanium crystallites have an average size of between 60 and 100 nm, since the reference fails to even mention titanium crystallites at all. Accordingly, Kato fails to suggest the coated substrate recited in Claim 26.

Claim 27 specifies, *inter alia*, (1) that the coating has contact angle with water below 5° after exposure to luminous rays and (2) that the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm. Kato is completely silent with respect to the contact angle of the coating and, therefore, fails to suggest a coating having a value below 5° as claimed. In addition, Kato fails to suggest that the titanium crystallites have an average size of between 60 and 100 nm, since the reference fails to even mention titanium crystallites at all. Accordingly, Kato fails to suggest the coated substrate recited in Claim 27.

Claim 28 specifies, *inter alia*, (1) that the coating has an RMS rugosity between 2 and 20 nm and (2) that the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm. Kato is completely silent with respect to the RMS rugosity of the coating and, therefore, fails to suggest a coating having a value between 2 and 20 nm. In addition, Kato fails to suggest that the titanium crystallites have an average size of between 60 and 100 nm, since the reference fails to even mention titanium crystallites at all. Accordingly, Kato fails to suggest the coated substrate recited in Claim 28.

In view of the foregoing, Kato fails to describe the coated substrate specified in Claims 26-28. Withdrawal of this ground of rejection is respectfully requested.

3. Claim 38 is Not Unpatentable under 35 U.S.C. §103(a) over Vandiest in View of Any One of Ito et al. (U.S. patent No. 4,664,934), Lynam et al. (U.S. patent No. 5,076,673) or Weppner et al. (U.S. Patent No. 5,202,788).

Claim 38 is directed to an electrically controlled variable absorption glazing wherein at least one of the external faces of said glazing is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

As discussed above (see section (1)), Vandiest fails to describe or suggest the claimed coated substrate. The cited secondary references are not asserted to address the deficiencies of Vandiest discussed above. Therefore, the secondary references, taken in combination with Vandiest, fail to suggest the claimed variable absorption glazing. Accordingly, withdrawal of this ground of rejection is respectfully requested.

4. Claim 39 Is Not Unpatentable Under 35 U.S.C. §103(a) Over Vandiest.

Claim 39 recites a windshield wherein at least the face of said windshield turned toward the inside of the passenger compartment is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

As discussed above (see section (1)), Vandiest fails to described the photocatalytic coating of the present invention. In addition, as noted by Dr. Guéneau above, the purpose of the coating described in Vandiest is to have low solar factor and a high purity of reflected color (see column 2, lines 13-17 of the reference). Vandiest fails to describe that the coating described therein is photocatalytic or hydrophilic. In addition, as recognized by the Examiner, the glazing described by Vandiest is to be used for architectural buildings and not as a windshield. See paragraph (23) of the Declaration. In view of these differences, the reference fails to suggest the claimed windshield. Accordingly, withdrawal of this ground of rejection is respectfully requested.

5. Claims 25-30, 34-37, 39 and 44-45 are Not Unpatentable Under 35 U.S.C. §103(a) over Plumat et al. (U.S. patent No. 3,984,591) in View of Any One of Vandiest or Kato.

Plumat et al. describe a process for forming a metallic oxide coating on a substrate. See the Abstract. As recognized by the Examiner, Plumat et al. fail to disclose a coating of titanium oxide in the anatase form that is photocatalytic. See page 9 of the Office Action dated February 21, 2006.

As discussed above, neither Vandiest nor Kato suggest the claimed coated substrate. Accordingly, the combination of Plumat et al. with either Vandiest or Kato fails to suggest the claimed invention. Withdrawal of this ground of rejection is respectfully requested.

6. Claim 38 is Not Unpatentable Under 35 U.S.C. §103(a) Over Plumat in View of Any One of Vandiest or Kato and in View of Any One of Ito, Lynam or Weppner.

As discussed above, the combination of Plumat et al. with either Vandiest or Kato fails to suggest the claimed invention. The cited secondary references fail to remedy that deficiency. Accordingly, those references fail to suggest the electrically controlled variable absorption glazing recited in Claim 38. Withdrawal of this ground of rejection is respectfully requested.

In view of the foregoing, the outstanding rejections should be reversed and the application passed to issue.

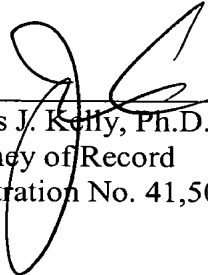
Respectfully submitted,

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CLAIMS APPENDIX

25. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by thermal decomposition of titanium precursors selected from the group consisting of organo-metallic precursors and metallic halide precursors, wherein said coating has a thickness between 5 and 50 nm, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

26. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having a photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and a thin layer forming a barrier to alkali metals originating from the substrate, and located between said substrate and said coating, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

27. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating is hydrophilic, and has a contact angle with water below 5 after exposure to luminous rays, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 1000 nm.

28. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating has a root mean square (RMS) rugosity between 2 and 20 nm, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

29. Glass, ceramic or vitroceramic substrate provided on at least one of its faces with a coating having photocatalytic properties and containing at least partially crystalline titanium oxide and having a thickness between 10 and 80 nm.

30. The glass, ceramic or vitroceramic substrate according to claim 29, wherein said thickness is between 20 and 50 nm.

34. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form, wherein said coating contains also at least one oxide with a lower refractive index than titanium oxide, the titanium content of the coating being at least 40%, by weight with respect to the total weight of oxides in the coating.

35. The coated substrate according to claim 34, wherein said titanium content is at least 50% by weight with respect to the total weight of oxides in the coating.

36. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form, wherein there is at least a layer arranged between the substrate and said coating, said layer being electrically conductive.

37. A coating according to claim 36, wherein the conductive layer is selected from the group consisting of indium tin oxide, tin oxide doped with fluorine, tin oxide doped with antimony, zinc oxide doped with fluorine, zinc oxide doped with aluminium, zinc oxide doped with tin, tin oxides that are stoichiometrically deficient in oxygen, and zinc oxides that are stoichiometrically deficient in oxygen.

38. An electrically controlled variable absorption glazing wherein at least one of the external faces of said glazing is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

39. A windshield wherein at least the face of said windshield turned toward the inside of the passenger compartment is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

44. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least one of its faces with a coating with photocatalytic properties, containing titanium oxide and doped by at least one metal selected from the group consisting of Nb, Ta, Fe, Bi, Co, Ni, Cu, Rh, Ce, and Mo.

45. The coated substrate according to claim 44, wherein the coating is deposited by reactive or non-reactive cathodic sputtering.

Application No. 09/923,353
Appeal Brief

RELATED PROCEEDINGS APPENDIX

None

EVIDENCE APPENDIX

1. First Rule 132 Declaration of Dr. Bernard Nghiễm, originally submitted on November 23, 2005.
2. Second Rule 132 Declaration of Dr. Bernard Nghiễm, originally submitted on May 22, 2006.
3. Rule 132 Declaration of Dr. Léthicia Guéneau, originally submitted on December 8, 2003
4. Carneiro et al., Study of the Deposition Parameters and Fe-Dopant Effect in the Photocatalytic Activity of TiO₂ Films Prepared by dc Reactive Magnetron Sputtering, *Vacuum*, 78, 2005, originally cited on May 22, 2006.



DOCKET NO: 211827US0CONT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

PHILIPPE BOIRE, ET AL. :

EXAMINER: A.T. PIZIALI

SERIAL NO: 09/923,353 :

FILED: AUGUST 8, 2001 :

GROUP ART UNIT: 1771

FOR: SUBSTRATE WITH A PHOTOCATALYTIC COATING

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VA 22313-1450

SIR:

Now comes Bernard Nghiêm who deposes and states that:

1. I hold the degree of "ingénieur" from the "Ecole Centrale de Paris" and I am a graduate of the Université Pierre and Marie Curie, Paris VI, Paris, France. I received my Ph.D. degree in 1998 in the field of "fracture of glass at the nanometric scale."
2. I have been employed by Saint-Gobain Recherche for the past 7 years, first as an "ingénieur" in the department "Transformation and Properties of Glass", and second, since 2001, as the leader of research group in charge of CVD in the department "Thin Coatings on Glass."
3. I have read and am familiar with United States patent 5,721,054, which names Vandiest et al. as inventors (hereinafter referred to as "Vandiest").
4. Vandiest describes the deposition of tin and titanium oxide coatings in accordance with its invention, as follows:

- Liquid tin tetrachloride or liquid titanium tetrachloride is vaporized and introduced in an inert carrier gas (e.g., nitrogen). The resulting mixture, at a temperature of 600°C is introduced in the reaction chamber through one nozzle.
- Water vapour, also at 600°C, is introduced into the reaction chamber through another nozzle.
- Both gas flows contact the substrate surface, where the temperature is between 550°C and 750°C.
- This mixture reacts on the substrate surface to form a tin oxide or titanium oxide coating thereon.
- The deposition tools and methods cited by Vandiest are described in French patent documents FR 2348166 and FR 2648453. The precursor ratio between SnCl_4 and water is described in English patent document GB 2026454. See column 5, lines 54-59 of Vandiest
- Vandiest provides no specific description of the gas composition to be used for the deposition of TiO_2 using TiCl_4 and water.

After closely examining the deposition procedure described by Vandiest, I believe that, while the conditions given by Vandiest can work well with a mixture of tin tetrachloride and water, this is not the case for titanium tetrachloride and water. On the basis of experiments I performed, I can confirm that for the deposition of titania, the use of the TiCl_4 and water ends up creating a nanoparticle powder and does not form a homogeneous coating on the substrate surface. The basis for so concluding is described in detail below.

The reaction of titanium tetrachloride with water is very well-known for creating powder in a fluid flow in order to study the hydrodynamics of the flow. Jensen et al¹ in their review chapter on flow studies within different CVD reactors mentioned the use of this reaction for the visualization of the specific flow patterns as a function of different adimensioned numbers. Because of the very high reactivity of TiCl_4 with water, this reaction could occur very rapidly even at ambient temperature. This reactivity increases when the gas temperature becomes higher. When the gases are at 600°C the reaction is instantaneous, and indeed, as mentioned by Vandiest, nanocrystals of TiO_2 anatase are formed, but essentially within the gas phase at the location where the two gas flows are encountering each other and *not on the surface of the substrate*, and the particles deposited on the glass substrate *do not form a real coating, only a "dust" of particles easily removed* with a tissue as discussed above.

Tool described in the patent FR 2648453:

It should be noted that in this patent, the authors mentioned the use of TiCl_4 for the deposition of titania but in conjunction with oxygen and not with water. Figure A (extracted from FR 2648453) is a schematic view of the double nozzle tool for the deposition of metal oxides. The main claim of this patent is the use of nozzles with an incident angle of the gas flow on the surface, which is lower than 45° to insure a non turbulent gas flow and the flow of a metal compound underneath the oxygen containing flow (claim 13). If such a configuration (in figure 3) is used with water and titanium tetrachloride, at the intersection region between the 2 flows from the 2 nozzles, nano powder is formed instead of a coating.

¹ Micheal L. Hitmann & Klavs F. Jensen, « Chemical Vapor Deposition principles and applications », pp. 50 to 53, Academic Press limited copyright © 1993.

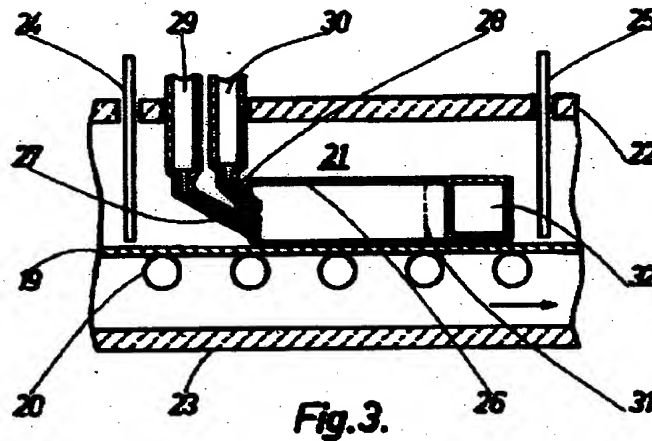


Figure A : scheme of the double nozzle claimed in the patent FR 2648453

Tool described in FR 2648453:

This patent was analysed but concluded to be less relevant because it concerns the use of a single nozzle with a good premixing of the precursors gases before they enter the deposition zone, instead of the double nozzle described by Vandiest.

This patent describes technology for the deposition of SiO_2 from SiH_4 and oxygen. The first claim concerns a very good mixing of both components before the deposition chamber. So if this kind of tool is used with TiCl_4 and water instead of SiH_4 and O_2 , a nano power should be formed before arriving on the substrate surface.

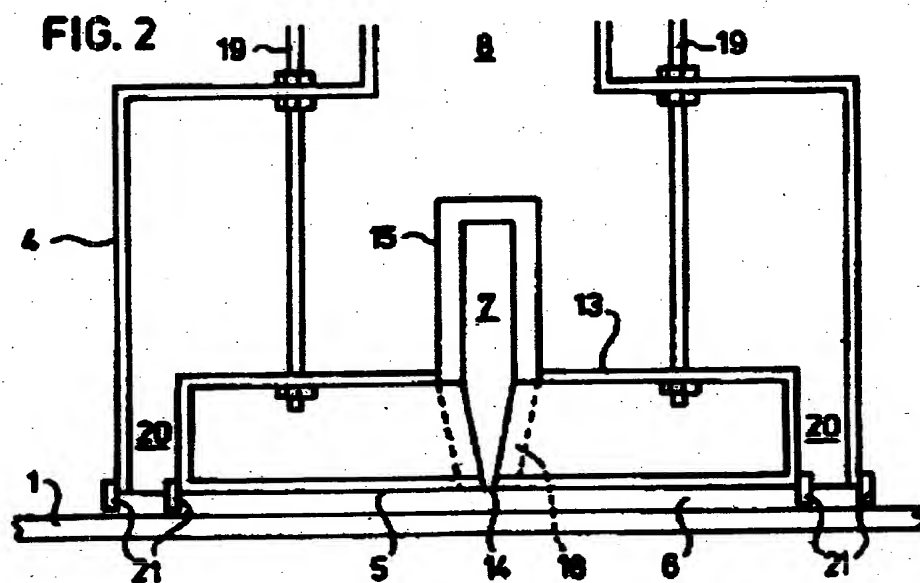


Figure B : Scheme of the nozzle for the deposition of SiO_2 from the patent FR 2648453

Experiments:

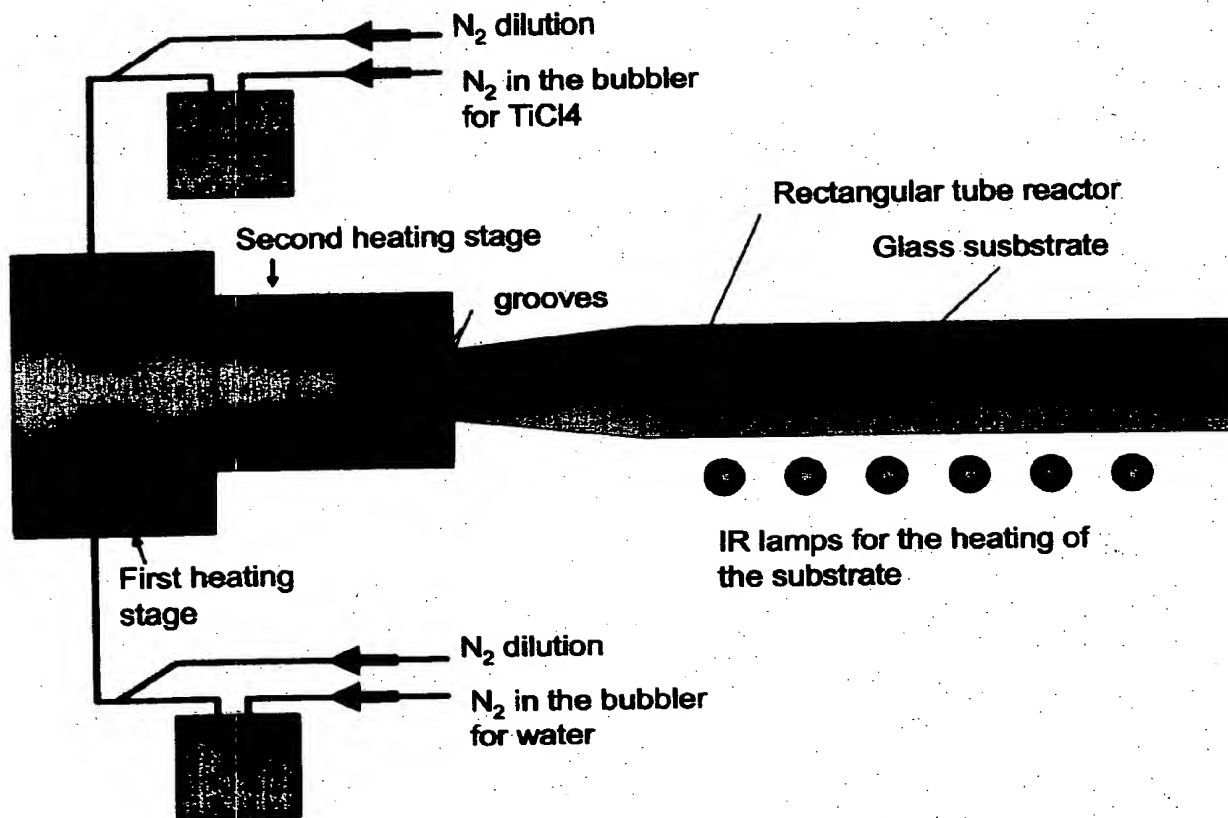


Figure C : schematic view of the CVD reactor

To reproduce the conditions of the deposition and the tool for the gas injection described by Vandiest and FR2648453, we used a CVD reactor with a static substrate as described in figure C. These experiments were conducted by me or under my supervision and control. This reactor is composed of a first furnace where the gases can be heated and a second shorter furnace to complete the heating of the gases. The two precursor gases are

injected into the reaction chamber through two horizontal grooves. The gas flow is parallel to the substrate surface which can be heated by IR lamps to a determined temperature.

Definition of the process parameters:

TiCl_4 is vaporized in nitrogen through a classical bubbler system. Nitrogen is injected through liquid TiCl_4 which is maintained at a constant temperature $T_{\text{TiCl}_4 \text{ bubbler}}$. The partial pressure at this temperature defines the amount of vapour of TiCl_4 that will be carried away by the nitrogen. $N_2 \text{ TiCl}_4$ is the flow rate of nitrogen through the bubbler. $N_2 \text{ dilution TiCl}_4$ is the flow rate of added nitrogen gas for the dilution.

The same system is used to inject water vapor in the nitrogen carrier gas. $T_{\text{water bubbler}}$ is the temperature of the bubbler. $N_2 \text{ water}$ is the flow rate of nitrogen through the bubbler. $N_2 \text{ dilution water}$ is the flow rate of added nitrogen gas for the dilution.

The gas lines are heated also by heating strings at the temperature $T_{\text{line } x}$ (X can be TiCl_4 or water)

Both gases are separately injected in different tubes surrounded by a first furnace where the contact time is high. T_{furnace} is the temperature of the first furnace

Then the gases pass through a second furnace where the contact time is shorter. $T_{\text{ring furnace}}$ is the temperature of the second furnace

The substrate is heated up to a determined temperature $T_{\text{substrate}}$, using IR lamps.

$t_{\text{deposition}}$ is the deposition time

2 types of substrate were used:

- Planilux (air side) which is the commercial soda lime glass produced by Saint Gobain
- Planilux coated with Antelio clear which is a $\text{FeO}_x \text{ CrO}_y \text{ CoO}_z$ coating

The table below summarizes the parameters we have used for the deposition of titania coating.

Parameters	Substrate : Planilux	Substrate : FeCrCoOx/Planilux
$t_{\text{deposition}}$	3 min	3 min
$T_{\text{substrate}}$	600°C	600°C
T_{furnace}	600°C	600°C
$T_{\text{ring furnace}}$	650°C	650°C
$T_{\text{line water}}$	60°C	120°C
$T_{\text{line TiCl}_4}$	50°C	120°C
$T_{\text{TiCl}_4 \text{ bubbler}}$	30°C	30°C
$N_2 \text{ TiCl}_4$	1 slm	1 slm
$N_2 \text{ dilution TiCl}_4$	2 slm	2 slm
$T_{\text{water bubbler}}$	40°C	40°C
$N_2 \text{ water}$	2 slm	2 slm
$N_2 \text{ dilution water}$	1 slm	1 slm

With the preceding condition water is largely in excess compared to titanium precursor as described in the GB patent noted above.

Results:

With the preceding deposition parameters, we could not deposit any real coating. Instead, we produced a powder, part of which weakly adheres to the surface of the substrate when the experiment was over. This powder can be easily wiped out by a tissue cloth.

Conclusion:

The process parameters described by Vandiest for the deposition of large gap semi conductor like SnO_2 or TiO_2 , starting from Ti or Sn tetrachloride with water as oxidant are only valid for the deposition of SnO_2 . In the case of TiO_2 , our own experiments and several scientific sources have proven clearly that even at low temperature TiO_2 powder is formed when TiCl_4 and water is brought into contact, instead of an homogeneous coating on the surface.

4. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

5. Further deponent saith not.

Bernard Nghiêm

14/05/05
Date





DOCKET NO: 211827US0CONT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

PHILIPPE BOIRE, ET AL. :

EXAMINER: A.T. PIZIALI

SERIAL NO: 09/923,353 :

FILED: AUGUST 8, 2001 :

GROUP ART UNIT: 1771

FOR: SUBSTRATE WITH A PHOTOCATALYTIC COATING

DECLARATION UNDER 37 C.F.R. § 1.132COMMISSIONER FOR PATENTS
ALEXANDRIA, VA 22313-1450

SIR:

Now comes Bernard Nghiêm who deposes and states that:

1. I am an Engineer of the "Ecole Centrale de Paris," and I am a graduate of the University Pierre and Marie Curie, Paris VI, Paris, France. I received my Ph.D. degree in 1998 in the field of "fracture of glass at nanometric scale."
2. I have been employed by Saint-Gobain Recherche for the past 7 years, first as first as an Engineer in the department "transformation and properties of Glass", and second, since 2001, as the leader of research group in charge of CVD in the department "Thin coatings on glass."
3. I am the same Bernard Nghiêm who submitted the Declaration Under 37 C.F.R. § 1.132 that was originally filed on November 23, 2005 in the above-identified application.
4. I have read and am familiar with the specification of the above-identified application, i.e., pages 1-30 of the application as it was originally filed.

5. I have also read and am familiar with the subject matter of claims 25-30, 34-39 and 44-45, a copy of which are attached hereto as Exhibit 1.

6. The subject matter of claims 25-30, 34-39 and 44-45 is, *inter alia*, a substrate coated with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

7. The specification provides a description of such coated substrates as follows:

The invention relates to glass-, ceramic- or vitroceraic-based substrates, more particularly made of glass, in particular transparent substrates, which are furnished with coatings with photocatalytic properties, for the purpose of manufacturing glazings for various applications, such as utilitarian glazing for vehicles or for buildings. [Page 1, lines 3-9; emphasis added.]

The object of the invention is a glass-, ceramic- or vitroceraic-based substrate, in particular made of glass and transparent, provided on at least part of at least one of its faces with a coating with a photocatalytic property containing at least partially crystalline titanium oxide. [Page 2, lines 10-1.]

It is obviously important for the coating to retain its integrity, even if it is directly exposed to numerous attacks, in particular during the fitting of the glazing on a building site (building) or on a production line (vehicle) which involves repeated handling by mechanical or pneumatic prehension means, and also once the glazing is in place, with risks of abrasion (windscreen wipers, abrasive rag) and of contact with aggressive chemicals (atmospheric pollutants of SO₂ type, cleaning products, and the like). [Page 2, lines 26-36; emphasis added.]

However, the coating of the invention, which is permanently self-cleaning, also preferably exhibits an external surface with a pronounced hydrophilic and/or oleophilic nature which results in three very advantageous effects.. [Page 6, lines 11-15; emphasis added.]

In conjunction with a hydrophilic nature, the coating can also exhibit an oleophilic nature which makes possible the "wetting" of the organic dirty marks which, as with water, then tend to be deposited on the coating in the form of a continuous film which is less visible than highly localized "stains". An "organic dirt-repellent" effect is thus obtained which operates in two ways: as soon as it is deposited on the coating, the dirty mark is already not very visible. Subsequently, it gradually disappears by radical degradation initiated by photocatalysis. [Page 7, lines 11-21.]

The invention is thus targeted at the manufacture of glass, ceramic or vitroc ceramic products and very particularly at the manufacture of "self-cleaning" glazing. The latter can advantageously be building glazing, such as double glazing (it is then possible to arrange the coating "external side" and/or "internal side", that is to say on face 1 and/or on face 4). This proves to be very particularly advantageous for glazing which is not very accessible to cleaning and/or which needs to be cleaned very frequently, such as roofing glazing, airport glazing, and the like. It can also relate to vehicle windows where maintenance of visibility is an essential safety criterion. This coating can thus be deposited on car windscreens, side windows or rear windows, in particular on the face of the windows turned towards the inside of the passenger compartment. This coating can then prevent the formation of condensation and/or remove traces of dirty finger mark, nicotine or organic material type, the organic material being of the volatile plasticizing type released by the plastic lining the interior of the passenger compartment, in particular that of the dashboard (release sometimes known under the term "fogging"). Other vehicles such as planes or trains can also find it advantageous to use windows furnished with coating of the invention. Page 11, line 24 to page 12, line 22; emphasis added.]

8. In view of the description provided by the specification of the above-identified application, one skilled in the art would have concluded that the coating of the invention described therein and specified in the claims identified above was mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing. That this is so is demonstrated by, *inter alia*, the fact that the coating is described as "permanently self-

cleaning." In order for the coating to have that property one skilled in the art would recognize that it must be mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing. In addition, if the glazing is to be used as part of a building or automotive windshield, one skilled in the art would have recognized that a powdered coating that could be wiped off would be essentially useless.

9. I acknowledge that the specification of the above-identified application does not contain explicitly state that the coating is mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing. However, for the reasons discussed above, one skilled in the art reading that specification would appreciate that the coating of the substrates specified in claims 25-30, 34-39 and 44-45 of the above-identified application necessarily had those properties in order to be used as a glazing in the specification.

10. Referring to my previous Declaration identified above, the process parameters described by Vandiest for the deposition of large gap semi conductor like SnO_2 or TiO_2 , starting from Ti or Sn tetrachloride with water as oxidant are only valid for the deposition of SnO_2 . In the case of TiO_2 , our own experiments and several scientific sources have proven clearly that even at low temperature TiO_2 powder is formed when TiCl_4 and water is brought into contact, instead of an homogeneous coating on the surface.

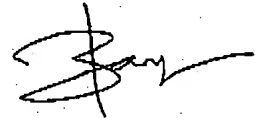
11. For those reasons, the process parameters described by Vandiest do not provide a coating of photocatalytic titanium oxide that is mechanically resistant and sufficiently adherent to the substrate in order to be used as a glazing as specified in claims 25-30, 34-39 and 44-45 of the above-identified application.

12. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under

Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

13. Further deponent saith not.

Bernard Nghiêm



Date

17/05/06

APPENDIX 1

25. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by thermal decomposition of titanium precursors selected from the group consisting of organo-metallic precursors and metallic halide precursors, wherein said coating has a thickness between 5 and 50 nm, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

26. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having a photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and a thin layer forming a barrier to alkali metals originating from the substrate, and located between said substrate and said coating, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

27. A coated substrate which is a glass, ceramic or vitroceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating is hydrophilic, and has a contact angle with water below 5 after exposure to luminous rays, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 1000 nm.

28. A coated substrate which is a glass, ceramic or vitroc ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating has a root mean square (RMS) rugosity between 2 and 20 nm, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 60 and 100 nm.

29. Glass, ceramic or vitroc ceramic substrate provided on at least one of its faces with a coating having photocatalytic properties and containing at least partially crystalline titanium oxide and having a thickness between 10 and 80 nm.

30. The glass, ceramic or vitroc ceramic substrate according to claim 29, wherein said thickness is between 20 and 50 nm.

34. A coated substrate which is a glass, ceramic or vitroc ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form, wherein said coating contains also at least one oxide with a lower refractive index than titanium oxide, the titanium content of the coating being at least 40%, by weight with respect to the total weight of oxides in the coating.

35. The coated substrate according to claim 34, wherein said titanium content is at least 50% by weight with respect to the total weight of oxides in the coating.

36. A coated substrate which is a glass, ceramic or vitroc ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form, wherein there is at least a layer arranged between the substrate and said coating, said layer being electrically conductive.

37. A coating according to claim 36, wherein the conductive layer is selected from the group consisting of indium tin oxide, tin oxide doped with fluorine, tin oxide doped with antimony, zinc oxide doped with fluorine, zinc oxide doped with aluminium, zinc oxide doped with tin, tin oxides that are stoichiometrically deficient in oxygen, and zinc oxides that are stoichiometrically deficient in oxygen.

38. An electrically controlled variable absorption glazing wherein at least one of the external faces of said glazing is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

39. A windshield wherein at least the face of said windshield turned toward the inside of the passenger compartment is provided with a coating having photocatalytic properties and comprising titanium oxide at least partly crystallized in the anatase form.

44. A coated substrate which is a glass, ceramic or vitroc ceramic substrate provided on at least one of its faces with a coating with photocatalytic properties, containing titanium oxide and doped by at least one metal selected from the group consisting of Nb, Ta, Fe, Bi, Co, Ni, Cu, Rh, Ce, and Mo.

45. The coated substrate according to claim 44, wherein the coating is deposited by reactive or non-reactive cathodic sputtering.

DOCKET NO.: 211827US0CONT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

Philippe BOIRE, et al.,

: EXAMINER: A. PIZIALI

SERIAL NO.: 09/923,353

FILED: August 8, 2001

: GROUP ART UNIT: 1775

FOR: SUBSTRATE WITH A PHOTOCATALYTIC COATING

DECLARATION UNDER 37 C.F.R. §1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VA 22313-1450
SIR:

Now comes Léthicia Guéneau who deposes and states:

1. That I am a graduate of Paris VI University (Orsay)
and received a PhD degree in the year 1998.
2. That I have been employed by Saint-Gobain Recherche for
8 years as a researcher in the field of Physico-Chemistry / Self-cleaning glass.
3. That I understand the English language or, at least, that the contents of the
Declaration were made clear to me prior to executing the same.

4. I have read and understood Vandiest, (U.S. patent No. 5,721,054).

5. Vandiest describes a glazing panel produced by pyrolytic coating of a
substrate (see the Abstract). The coating contains an absorbent layer comprising at least one
oxide selected from chromium, cobalt, and iron. The coating also contains a non-absorbent
layer which comprises a material having a refractive index within the range of 1.4 to 3.0 (see
the Abstract). The purpose of the coating is to have low solar factor and a high purity of
reflected color (see column 2, lines 13-17). Vandiest fails to describe that the coating

described therein is photocatalytic or hydrophilic. In addition, Vandiest fails to describe that TiO_2 is crystallized in the anatase form.

6. In Example 2, Vandiest describes a glass substrate coated with a 41 nm TiO_2 layer, which, in turn, is coated with a layer of Fe, Co, and Cr oxides having a thickness of 45 nm.

7. In Example 3, Vandiest describes a glass substrate coated with a 85 nm TiO_2 layer, which, in turn, is coated with a layer of Fe, Co, and Cr oxides having a thickness of 46.5 nm.

8. Fe, Co, and Cr oxides are well-known to be poisons for photocatalysts. Therefore, one of ordinary skill in the art would limit the contents of those metal oxides because of their known properties as photocatalyst poisons.

9. I have read and understood Teowee, U.S. patent No. 5,604,626.

10. Teowee describes a photochromic device which allows a user to leave the device in a high transmissive state even when exposed to a source of radiation (see the Abstract). The device contains a radiation sensitive electrode 30 (see columns 7 and 8). Teowee fails to describe that the coating described therein is photocatalytic or hydrophilic.

11. In addition, the absence of a binder, especially in Example 1, leads to coatings with very low mechanical strength. Moreover, the operation involves heating to 450°C or 350°C, and, in the absence of a barrier layer, does not result in effective photocatalyst.

12. I have read and understood Kato, U.S. patent No. 6,284,314.

13. The thickness of the coatings described by Kato is much greater than 50 or 80 nm. In the Examples of that reference, the coating thickness is 400 nm (Example 1), 500 nm (Example 2), 300 nm (Example 3), 400 nm (Example 4), 600 nm (Example 5), 400 nm (Example 6), 800 nm (Example 7), 600 nm (Example 8), 0.5 μm (Example 9), 0.4 μm

(Example 10), 0.3 μm (Example 11), 0.5 μm (Example 12), 0.4 μm (Example 13), and 0.8 μm (Example 14). Thus, the thinnest coating described in the reference is 300 nm.

14. In describing the procedure for preparing the coating, Kato states:

it is desirable to produce a multilayer film by repeating a procedure which comprises depositing thinly and uniformly the ceramic sol...on a substrate...thereby forming a thin film of the solution on the substrate.... As a result, a sturdy porous ceramic thin film excellent in durability can be obtained. [Column 3, lines 33-42.]

15. Kato is completely silent regarding the size of titanium oxide crystallites.

16. Kato fails to describe the contact angle or the root mean square (RMS) rugosity of the coating.

17. There is no suggestion in Kato to produce a coating having a thickness which is 5 to 80 nm. Kato specifically directs one to prepare a coating using a multiple dipping technique, which would not suggest a coating that was only approximately 1/4 the thickness of the thinnest coating described in the reference. Kato certainly fails to suggest a coating which is 5 to 50 nm, which is only 1/6 as thick as the thinnest coating described in that reference.

18. Kato fails to suggest that the titanium crystallites have an average size of between 60 and 100 nm, since the reference fails to even mention titanium crystallites at all.

19. Kato does not identify a layer which functions as a barrier to alkali metals originating from the substrate, nor does the reference suggest that such a component would be desirable.

20. Kato is completely silent with respect to the contact angle of the coating.

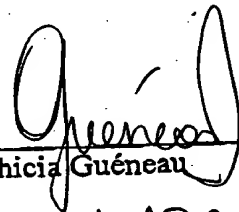
21. Kato is completely silent with respect to the RMS rugosity of the coating and, therefore, fails to suggest a coating having a value between 2 and 20 nm.

22. In addition, Kato describes the optional heating of solutions coated on substrates in the absence of a barrier layer to alkalis, such as sodium from the substrate. Quartz glass substrates are described, which consist of SiO_2 , and do not contain alkalis.

23. As discussed above, the purpose of the coating described in Vandiest is to have low solar factor and a high purity of reflected color (see column 2, lines 13-17 of the reference). Vandiest fails to describe that the coating described therein is photocatalytic or hydrophilic. In addition, the glazing described by Vandiest is to be used for architectural buildings and not as a windshield.

24. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

25. Further deponent saith not.


Léthicia Guéneau

3rd of December, 2003
Date



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Study of the deposition parameters and Fe-dopant effect in the photocatalytic activity of TiO₂ films prepared by dc reactive magnetron sputtering

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Abstract

The reactive magnetron sputtering method was used to prepare pure and Fe-doped titanium dioxide thin films. The films were deposited onto microscope glass slides and polycarbonate plates at different total pressure and Fe-doping concentrations. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV-visible spectroscopy (UV). For glass substrates a polycrystalline TiO₂ structure was verified with X-ray diffraction, which showed typical characteristic anatase reflections. An iron phase appeared in the highly Fe-doped samples. The absorption edges of the Fe-doped TiO₂ films shifted to visible region with increasing concentration of iron. For the polycarbonate substrate an amorphous TiO₂ structure was revealed for all deposition conditions. The effects of different Fe-doping and total pressure levels on the photocatalytic activity were obtained by the degradation rates of Rhodamine-B (RoB) dye under UV light irradiation. For the deposition conditions considered in this study the highest photodegradation rates were achieved for films deposited on the polymer substrates. Of these overall highest rates was achieved for deposition at 0.4 Pa and without doping. However, for both substrates, films prepared at the particular total pressure of 0.5 Pa and a low iron concentration showed better photocatalytic activity than the pure TiO₂ films prepared under the same deposition parameters. On the contrary, the photocatalytic degradation rates of RoB on the highly Fe-doped TiO₂ films decreased strongly.

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Keywords: Photocatalytic TiO₂ films; Fe-doping effect; Magnetron sputtering; Polycarbonate

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1. Introduction

In recent years, intense investigation has been performed on the TiO_2 -assisted photochemical degradation of organic substances by UV radiation, either with the semiconductor catalyst in suspension or immobilized on a solid support to avoid further separation processes [1–11]. The method was originally contemplated as a possibility to employ solar radiation as an energy source in water decontamination processes in association with the treatment of industrial effluents (to avoid environmental damage) and water potabilization [5,11]. At a certain stage, studies have markedly shifted towards the use of artificial UV sources, mainly mercury vapour lamps, because of the low efficiency obtained with the solar radiation, the practical inconvenience of having to rely on the unpredictable availability of a natural light source and the poor overlapping of the solar spectrum with the TiO_2 absorption range [7].

Titanium dioxide occurs in three crystalline forms (rutile, anatase, and brookite), among which anatase is believed to be the most efficient photocatalyst during chemical reactions [12,13]. Most of the studies were focused on the nanosized TiO_2 in order to improve the light absorption: the high surface-to-volume ratio of nanograins is useful as has been reported in the literature [14]. Moreover, increasing the generation rate of charge carriers is one way to enhance the photocatalytic activity. This is centred on the formation of an electron–hole pair, respectively (e^-) and (h^+), on the TiO_2 surface upon the incidence of a photon with energy equal to or higher than the gap between the valence and the conduction band within the semiconductor crystal. On the other hand, electron and hole trapping during their movement from the interior of the particle to the surface is also very important for preventing the recombination of electron hole pairs. Doping of TiO_2 with transition metal ions [15] gives a way to trap charge carriers and extend the life time of one or both of the charge carriers.

TiO_2 films have been prepared by a variety of deposition techniques such as sol–gel process, colloid baking, chemical vapour deposition, evaporation and various reactive sputtering deposi-

tions [16–18]. The aim of this research is to study the effect of some deposition conditions such as, the total deposition pressure and the amount of Fe-metal dopant on the efficiency of the photocatalytic process of TiO_2 thin films prepared by dc reactive magnetron sputtering (MS). MS can be used to prepare good quality films because it is a friendly environment industrial process which can be applicable to large-area deposition or even when large-scale production is needed.

Moreover, it must be noted that polymers have gained substantial interest as base materials in current industry. Polycarbonate is one of the newer thermoplastics used in the construction industry and in many automotive applications due to its excellent properties of impact resistance, low weight and transparency. Building roofs, building windows, car roof elements, automotive headlamps, cameras, ophthalmic lenses, optical sensors and other optical equipment are all convincing technological products which highlight the application of polymeric materials in industry. However, photocatalytic properties of TiO_2 films deposited on polycarbonate have rarely been reported in physical vapour deposition (PVD) industry.

2. Experimental procedure

Fig. 1 shows the schematic of a home made MS system used in the preparation of our TiO_2 films. The films were deposited both on glass and on polycarbonate slides ($75 \times 25 \times 1 \text{ mm}^3$). A 99.99% pure titanium target with a diameter of 10 cm and a total area (TA) of about 7854 mm^2 was used. The distance between target and substrate was 60 mm.

After the chamber was evacuated to a base pressure lower than $1 \times 10^{-3} \text{ Pa}$, a 99.99% pure argon sputtering gas was introduced into the chamber and discharge began at a constant current of 0.2 A. After the discharge voltage stabilized at a low value, 99.5% pure oxygen gas was introduced into the chamber at a constant oxygen flow rate of 2.5 ml/min to participate in the chemical reaction to form TiO_2 . Titanium dioxide thin films were prepared at two different total sputtering pressures, that is 0.4 and 0.5 Pa. The reason why this

small pressure range was chosen is concerned with the objective to investigate the photocatalytic sensitivity of TiO_2 films (translated by eventual changes in the photodegradation rate) deposited under small variations in total sputtering pressure. For all films, an average film thickness of about 600 nm (evaluated by SEM) was obtained by changing the deposition time under different total sputtering pressure.

The iron pieces ($5 \times 5 \times 0.2 \text{ mm}^3$) with purity of 99.9% were placed on the titanium target in order

to promote the film doping effect. The colour of the films changed from light white to light yellowish and finally to dark yellowish following the sequence from pure titanium dioxide to the higher iron concentration. The typical deposition parameters and the iron piece area (IpA) used for doping TiO_2 films are shown in Table 1.

X-ray diffraction (XRD) analysis was carried out for all samples. XRD 2θ scans were recorded by using CuK_α radiation source in a Philips PW 1710 BASED diffractometer for the characterization of the crystalline structure of the undoped and doped TiO_2 samples. Specific software was used to measure the precise 2θ positions and the full-width at half-maxima (FWHM) of the diffraction peaks. The crystalline grain size was calculated from the XRD pattern according to the Scherrer equation [18].

$$D_{hkl} = 9.94 \lambda / B_{hkl} \cos \theta \quad (1)$$

where D_{hkl} is the mean grain size with crystalline planes (hkl), B_{hkl} is the FWHM intensity in radians and λ is the wavelength of the CuK_α radiation source. The surface morphology of the films was observed by SEM in a LEICA Cambridge S360 instrument and AFM in a NANOSCOPE III, Digital instruments. The thickness of the films was evaluated by SEM. The optical transmission spectra of the films were measured with a Shimadzu UV-310PC scanning spectrophotometer.

The photocatalytic activity of undoped and Fe-doped TiO_2 thin films was characterized with the decomposition rate of an aqueous solution of Rhodamine-B on the films by UV irradiation. Rhodamine-B ($\text{C}_{20}\text{H}_{12}\text{ClN}_2\text{O}_3$) is a strongly red fluorescent dye with a molecular weight of 479. It is a chloride salt that dissociates in aqueous

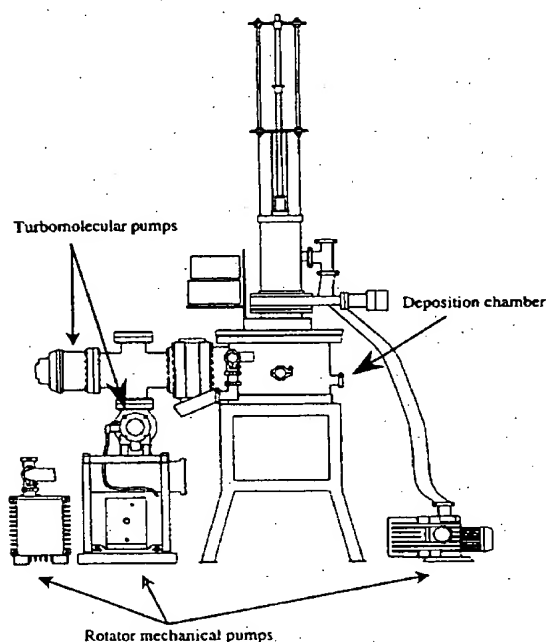


Fig. 1. Schematics of reactive magnetron sputtering system for coating deposition.

Table 1
Deposition parameters and iron piece area on titanium target in the deposited TiO_2 films

Code sample	A	B	C	D
Iron piece area: IpA (mm^2)	—	—	50	200
(Iron piece/titanium target) ratio area: (IpA/TA) %	—	—	0.64	2.5
Ar flow rate (ml/min)	17.4	19.0	19.0	19.0
Total pressure- P_{total} (Pa)	0.4	0.5	0.5	0.5

solution, leaving a positive charge on one of the nitrogens. In each run, a TiO_2 film of $1.0 \times 1.5 \text{ cm}^2$ was placed in a quartz cell probe, which contained 10 ml aqueous *RoB* solution with a concentration of 0.5 mg/l. The UV source was a mercury tube lamp irradiating a wavelength of 254 nm. The film was irradiated in a perpendicular direction and the distance between the film and the UV source was 11 cm. The photodegradation efficiency was monitored by measuring transmittance at the wavelength of 554 nm using a Shimadzu UV-310PC scanning spectrophotometer. The transmittance of the solution was measured at 15 min intervals for a total irradiation time of about 90 min.

3. Results and discussion

3.1. Structural characterization

In Fig. 2 we present the evolution of TiO_2 film X-ray spectra for the samples prepared with different deposition parameters and deposited on the glass substrate.

It can be observed that crystallinity of our films increases for the lowest pressure values. Only the anatase phase was identified in the undoped films. The polycrystalline anatase structure was con-

firmed by the (101) and (004) diffraction peaks, and also the traces of (200), (105) and (211) peaks. However, they had the preferred orientation of the anatase (004) plane, although the intensity was lower for the pure TiO_2 deposited at higher pressures. For samples with addition of dopant, the films had an amorphous structure.

There were no Fe-dopant-related peaks in the XRD patterns for sample C. The Fe_3O_4 phase appeared in sample D, which contained the higher iron concentration. Based on the full width at half maxima of the XRD peaks, the average particle diameter was calculated to be about 4.1 ± 1 and 7.1 ± 1 nm respectively for samples A and B. For all samples deposited on the polycarbonate substrate only an amorphous structure was apparent from the XRD spectra.

3.2. Surface characterization

The evolution of the surface with deposition conditions was followed by SEM and AFM techniques, respectively. SEM micrographs show images of the surface morphology of the pure TiO_2 films deposited at different total pressures in the sputtering deposition chamber [see Fig. 3(a)–(b)]. The films were mainly composed of small spherical particles. The surfaces of the films exhibited a certain degree of roughness and the film became rougher when total pressure was higher during deposition.

Atomic force micrographs presented in Fig. 4(a)–(b) come, respectively, from the pure titanium dioxide (sample B) and the Fe-doped TiO_2 (sample D) in which iron area percentage (IpA/TA) was equal to 2.5%.

An increase in surface roughness (at nanometre level) and size of the top columnar growth with lower structural densification is observed for the higher Fe-doped sample D. The iron went into substitutional sites of the TiO_2 crystal structure. The position of the dopant is determined by size differences between the host Ti^{4+} ionic radius and the dopant ionic radius. From the effective radius of ions for a coordination number 6 [19], one can see that Fe^{3+} ion has a small ionic radius (0.645 Å) that is comparable to that of Ti^{4+} (0.605 Å). Thus, it is energetically favourable for this ion to

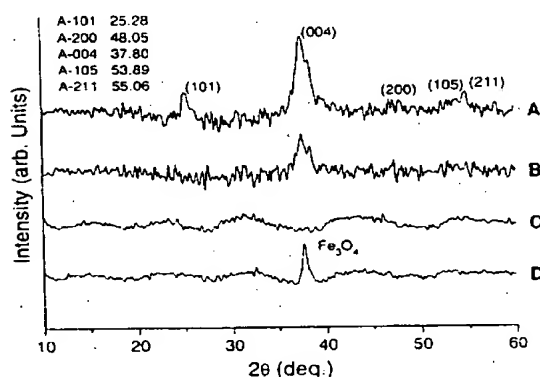


Fig. 2. XRD patterns of undoped and Fe-doped TiO_2 films deposited on glass. The deposition conditions A, B, C and D are given in Table 1.

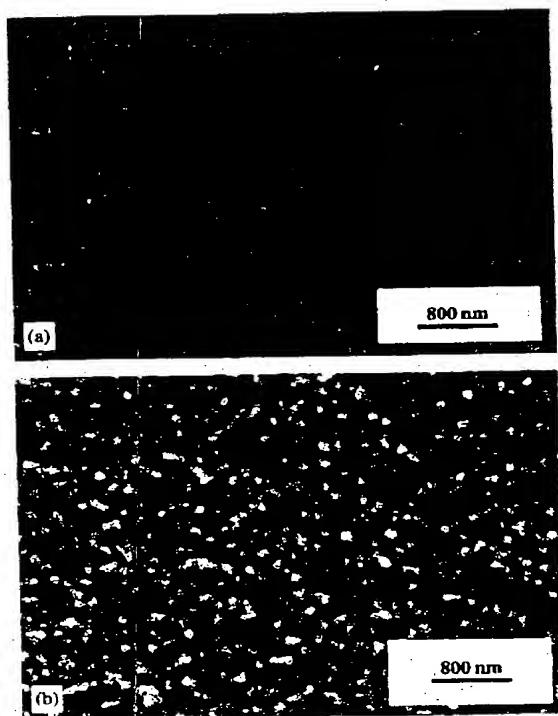


Fig. 3. SEM images of pure TiO_2 films: (a) sample A, (b) sample B.

occupy Ti^{4+} sites. However, if the iron concentrations are far more than its solubility in TiO_2 then an iron oxide surface enrichment is expected, leading to the formation of bigger particles and surfaces with higher roughness.

3.3. Photocatalytic activity

The photocatalytic mechanism is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO_2 ($\approx 3.23 \text{ eV}$ in anatase phase) [1–8] producing an electron–hole pair on the TiO_2 surface as schematized in Fig. 5.

An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). In order for this process to have a net chemical effect, the volume recombination of the electron–hole pair has to be precluded. The natural fate for $h\nu_{\text{VB}}$ and e_{CB}^- is the removal of

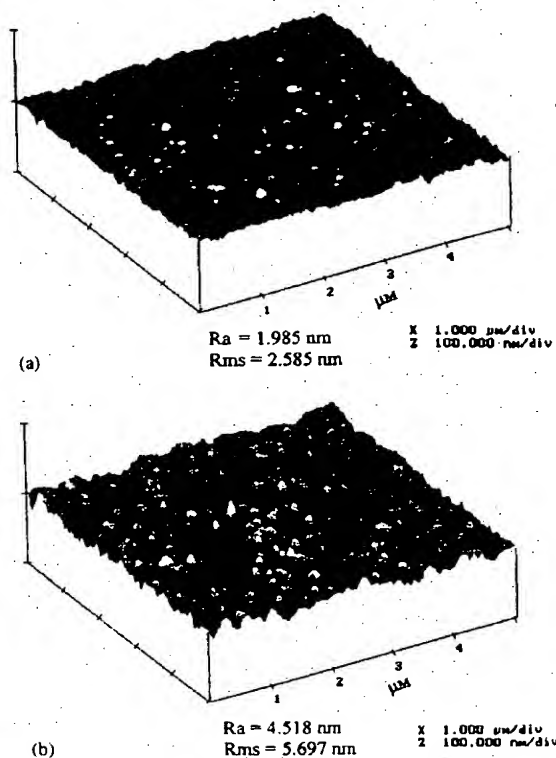


Fig. 4. AFM images of pure and Fe-doped TiO_2 films: (a) sample B, (b) sample D.

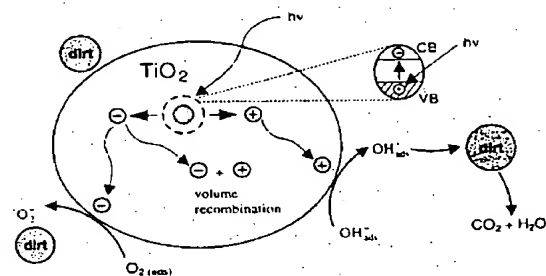
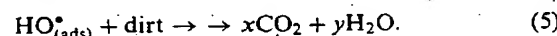
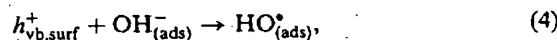


Fig. 5. Initial redox events subsequent to hole and electron trapping.

either of them by means of redox reactions involving the organic compounds adsorbed on the semiconductor surface. The standard chemical

reactions have been reported by other authors [20,21]:



Hydroxyl radicals (HO^\cdot) and super-oxide ions (O_2^-) are highly reactive species that will oxidize the organic compounds adsorbed on the semiconductor surface. The number and lifetime of free (e^-/h^+) pair are particle size and dopant-dependent [22]. For large particles, the (e^-/h^+) volume recombination is the dominating process. In fact, for small sized particles the covered distance by (e^-/h^+) pair during their movement from crystal interface to the surface is short, which increase the migration rate to the surface of the small size particle in order to participate in the chemical reaction. Besides the effect of particle size on the photocatalytic activity, the role of a metal ion dopant is also very important because it can act as an electron trap in the semiconductor interface. The trap of charge carriers can decrease the volume recombination rate of (e^-/h^+) pairs and thus increase the lifetime of charge carriers. The process of charge trapping is as follows [22]:



where M^{n+} is the metal ion dopant. The energy level of $\text{M}^{n+}/\text{M}^{(n-1)+}$ lies below the CB edge. Thus, the energy level of transition metal ions affects the trapping efficiency. The trapping of electrons makes it easy for holes to transfer onto the surface of TiO_2 and react with OH^- in the surface and form active $\cdot\text{OH}$, hydroxyl radicals to participate in the degradation of dirt.

Fig. 6(a)–(b) shows the optical transmittance spectra of the series of TiO_2 thin films deposited, respectively, on glass and polycarbonate substrates.

In the visible range the transmission of spectra shows waveforms that are characteristic of light interference [23]. For both substrates, the absorption edges of Fe-doped TiO_2 films shifted to long

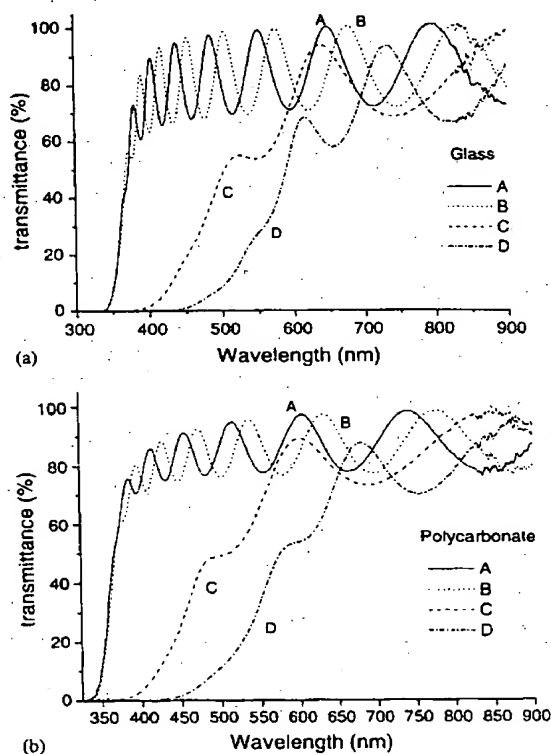


Fig. 6. UV-vis spectra of pure and Fe-doped TiO_2 films prepared by dc reactive magnetron sputtering at different total pressures. On different substrates: (a) on glass and (b) on polycarbonate.

wavelength when the amount of Fe-dopant increased, as shown in Fig. 6(a) and (b). This red shift has been attributed to the excitation of $3d$ electrons of Fe^{3+} to the CB [24]. In fact, the main purpose of Fe doping is to extend the light absorption edge in order to make use of the majority of the ambient light spectrum. The absorption edge of sample C shifted to 380 nm near to the visible region and the sample D shifted to 450 nm in the visible region.

The influence of different total pressures in the photocatalytic activity of the series of pure TiO_2 thin films (deposited on glass and polycarbonate substrates) were examined and are shown in Fig. 7(a) and (b).

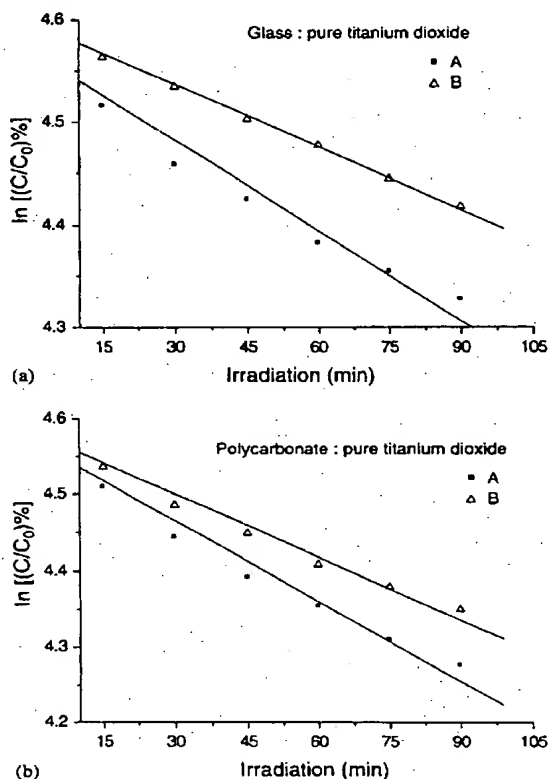


Fig. 7. Effect of different total pressures in the photocatalytic degradation of *RoB* dye on the pure TiO_2 films deposited on different substrates: (a) on glass and (b) on polycarbonate.

The photodegradation of *RoB* dye follows the kinetic first-order reaction [25]:

$$\ln \frac{C}{C_0} = -kt, \quad (7)$$

where C_0 is the initial concentration of *RoB* aqueous solution, C is the concentration measured at the end of a particular interval of time, and k is the apparent photodegradation rate constant.

The Photocatalytic activities can be compared by using k values which can be obtained from the slopes of the fitting lines in Fig. 7. It is observed that, for both substrates, the photocatalytic activity of the undoped TiO_2 films deposited at

the lower total sputtering pressure (0.4 Pa) is increased. Possible explanations could be based on the difference of the TiO_2 particle sizes which were obtained under different total sputtering pressures. In fact, the measured grain sizes were 4.1 ± 1 and 7.1 ± 1 nm, respectively, for samples A (deposited at 0.4 Pa) and sample B (deposited at 0.5 Pa). Thus, this indicates that smaller particles enhance the photocatalytic activity, consistent with the findings of other authors [22]. In fact, as the grain size is decreased the surface-to-volume ratio is increased; the transportation length of the e^-/h^+ pair from crystal interface to the surface is short and the e^-/h^+ volume recombination rate is decreased which would lead to an improvement in the photocatalytic activity.

Fig. 8(a) and (b) is the comparison of the *RoB* dye photodegradation activity for pure and Fe-doped TiO_2 samples with different iron concentrations and deposited at the same total pressure (0.5 Pa).

For both substrates the change of the photocatalytic activity for Fe-doped samples is evident from the slopes of the photodegradation curves. When compared with the pure TiO_2 films (samples B) the photodegradation rates of the moderate Fe-doped TiO_2 films (samples C) have been slightly enhanced. On the contrary, high iron concentration (samples D) was detrimental for photocatalytic activity as evidenced in Fig. 8(a) and (b) by the lower gradient slopes of the fitting curves. Fig. 9 plots the numerical values of the apparent photodegradation rate constant for all TiO_2 thin films deposited on glass and polycarbonate substrates.

From Fig. 9 it can be seen that, for both substrates and for all TiO_2 samples (i.e. prepared with different deposition conditions), the photocatalytic degradation rates of *RoB* dye on the highly Fe-doped TiO_2 films decreased abruptly with increase in iron concentration (samples D). The optimum Fe-doping concentration can be explained by the balance of an increase in trapping sites leading to efficient trapping and fewer trapped carriers leading to longer lifetimes for interfacial charge transfer [26]. At concentrations below the optimum value, photocatalytic activity should increase with an increase of the iron

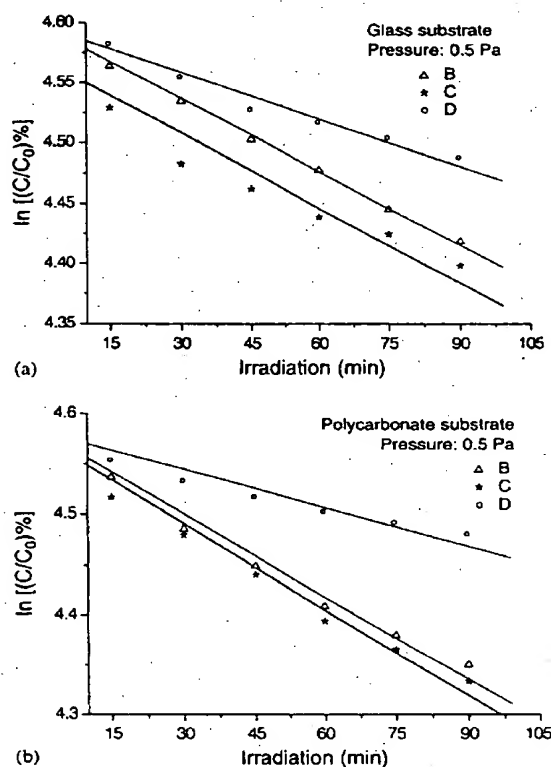


Fig. 8. Photodegradation of RnB dye with undoped TiO_2 and Fe-doped TiO_2 under UV light source: (a) on glass substrate and (b) on polycarbonate substrate.

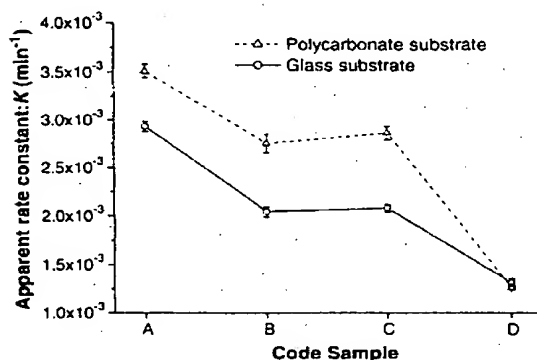


Fig. 9. Apparent photodegradation rate constant k for all TiO_2 thin films prepared under different deposition conditions. Comparison between glass and polycarbonate substrates.

concentration because there are fewer trapping sites available. However, if the iron concentration is far more than its solubility in the TiO_2 structure then a decrease in photocatalytic activity should be expected as was observed.

It is also observed that for all TiO_2 thin films, the highest photodegradation rates were achieved for films deposited on the polycarbonate substrates in spite of their amorphous structure. Moreover, from our spectra transmittance results it can be observed that there is a wavelength range from about 350 nm to near visible region in which transmittance varies from about 10–70%. Thus, under this wavelength band our coatings do not absorb all the UV radiation. We believe that it can be possible that one fraction of transmitted UV radiation could promote some changes in the type of PC polymer molecular arrangement leading to an eventual enhancement in the photocatalytic activity. In spite of this, it is not yet clearly understood for us the main mechanisms under which the observed photocatalytic activity is stronger for films deposited on polycarbonate.

4. Conclusions

Transparent and uniform undoped and Fe-doped TiO_2 thin films were deposited on glass and polycarbonate substrates by dc reactive magnetron sputtering using different deposition parameters. The TiO_2 films deposited on the glass substrate showed the anatase crystal phase with a preferred orientation along the (004) plane. When the total pressure increased the intensity of the (004) peak decreased. The decrease of the 004 peak can be related with the mobility of the adatoms on the substrate surface that is lower for higher deposition sputtering pressure which in turn affects the type and rate of nucleation on the substrate leading to a different crystallinity. The grain sizes were 4.1 and 7.1 nm for the pure TiO_2 films deposited at total pressures of 0.4 and 0.5 Pa, respectively. On the contrary, for TiO_2 films deposited on the polycarbonate substrate an amorphous structure was observed.

The surface morphologies of the undoped and Fe-doped films changed from slight roughness to

rough, for undoped to highly Fe-doped TiO_2 films, respectively. For both substrates the absorption edges of the Fe-doped TiO_2 films shifted to longer wavelength up to visible region when the concentration of iron increased.

For undoped TiO_2 films, the aqueous Rhodamine-B degradation rate was enhanced when the total pressure on the deposition chamber decreased to 0.4 Pa. At this deposition pressure, the grain size is lower than that obtained at 0.5 Pa. For lower grain sizes, the transportation length of e^-/h^+ pairs from crystal interface to the surface is short resulting in an increase of the migration rate of e^-/h^+ pairs to the surface of the particle in order to participate in the reaction process. This could lead to an enhancement of the photocatalytic activity.

For both substrates, the films with the moderate iron concentration showed better photocatalytic activity than the pure TiO_2 film deposited under the same total pressure of 0.5 Pa. On the contrary, high iron concentration was detrimental for photocatalytic activity.

From our results, the photocatalytic activity was stronger for TiO_2 films (undoped and Fe-doped) deposited on the polycarbonate substrates since the photodegradation rates had an average increase of about 30%. Besides the possible UV radiation effect on changing the PC polymer molecular arrangement, we believe that another effect can contribute to the enhancement of photocatalytic activity. This effect can be related with the temperature increase and local structural changes on the PC polymer surface due to the electron and ion bombardment during the initial deposition steps. In fact, for the same volume, polycarbonate has lower mass and subsequently the PC surface might be at a higher temperature than the glass in the same deposition conditions. However, the nature of these interactions effects in the enhancement of the photocatalytic activity in coated polycarbonate is not yet clearly understood for us. Thus, further studies are necessary to perform for a fully understanding of the main mechanisms that are responsible for the enhancement of the observed photocatalytic activity in coated polycarbonate. Consequently, this study led us to the deposition of transparent TiO_2 films

on polycarbonate with improved photocatalytic activity, which opens more perspectives for the industrial application of polymers as a low weight "self-cleaning" material.

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